High magnetic field-induced insulating phase in an organic conductor

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We report electrical transport, skin depth, and magnetocaloric measurements in the τ-phase series of organic conductors at very high magnetic fields. Above 36 T these materials show a magnetic field induced first order phase transition from a metallic to an insulating state. The transition, which is a bulk thermodynamic phenomenon, does not follow the conventional prescription for field induced phase transitions in organic conductors.

In low-dimensional metals, high magnetic fields often act to reduce the effective dimensionality, thereby inducing a metal-to-density wave state[1]. This is most evident in quasi-one dimensional Bechgaard and related organic salts [2] [3]. Even in the case of quasi-two dimensional materials, the magnetic field plays an important role in determining the ground state properties. [4] [5] In such cases the interaction of the magnetic field with the electronic structure is generally orbital in form, and the magnetic field induced phases are therefore dependent on field direction due to the low dimensional topology of the Fermi surface. In marked contrast to conventional Fermi surface nesting behavior, we present a description of a new type of field induced metal-to-insulator transition in an organic metal.

Our main experimental result is the universal behavior of the resistance of all isostructural members of the τ-phase class of organic conductors [6, 7] in very high ($B > 36T$) magnetic fields. Here we find a first order metal-to-insulator transition above a temperature-dependent and hysteretic threshold field, B_{th}. An overview of the field-temperature phase diagram of these materials is shown in Fig. 1. What is remarkable about this transition is that B_{th} appears to be only weakly dependent on magnetic field direction. Hence the mechanism that drives the transition at B_{th} may be primarily isotropic, or Zeeman-like in origin, and we must look for other physical characteristics of these materials which cause this dramatic transition to the insulating state. The purpose of this paper is to provide complementary electrical transport and bulk thermodynamic information to describe this unconventional magnetic field induced insulating state.

The complexity and structure of the τ-phase unit cell is unique amongst the general class of charge transfer salts (CTS) [8]. Unlike conventional CTS materials with
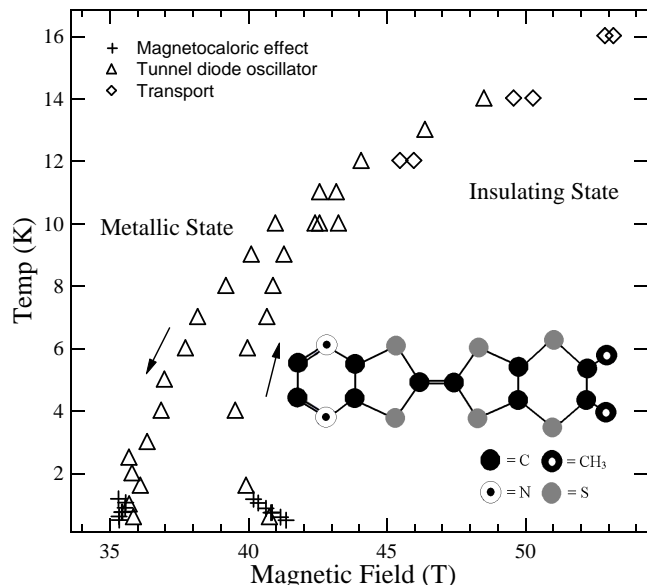

FIG. 1: Schematic high field phase diagram of the τ-phase organic conductors based on the P-DMEDT-TTF donor molecule with nitrogen at the indicated sites (Fig. 1 inset). The threshold field B_{th} for the high field phase boundaries shown for $\tau(r)$-AuBr$_2$ is based on magnetoresistance, ac skin-depth, and magnetocaloric data. Arrows indicate the up-sweep and down-sweep data.

a charge transfer ratio of 2:1, here it is 2:(1+y)(where $y \approx 0.75$) and the anions occupy two different sites in the unit cell. A 2:1 ratio does exist in each conducting layer as (AuX$_2$) (where X = Br and I) linear anion lies along the c-axis amongst a square array of P-DMEDT-TTF donors. The (AuX$_2$)$_y$ anions are arranged in the inter-layer ab-planes where their orientation alternates by 90° between layers. Since P-DMEDT-TTF is asym-

metric (see Fig. 1 inset), the donor stacking involves alternating directions within the each successive layer. Hence, due to the very low symmetry of the donor and anion arrangement, four donor layers are necessary to complete the unit cell[7], and the result is an unusually large inter-planar dimension: $(a, b, c \approx 7.4, 7.4, 68 \ \mathring{A})$. τ-(P-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-(S,S)-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ (hereafter referred to as τ-AuBr$_2$ and τ-AuI$_2$, respectively) are completely analogous except for the replacement of bromine for iodine in the anions. The prefix P refers to the pyrazino (N-N) configuration of the P-DMEDT-TTF donor molecule. Normally the salts of these structures are flat, but an uneven hexagonal ring results when oxygen atoms (O-O) replace nitrogen to produce τ-(EDO-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (referred to here as τ-EDO). The direction of the twisting of these rings is irregular making the EDO sample disordered. Further disorder can be introduced into the τ-phase system with a racemic mixture of two isomers(R,R <u>and</u> S,S) of the donor molecules [9, 10]. These isomers differ only in the positions of the methyl groups with the adjoining chiral centers. In general the ratio of the two isomers is not 1:1, and this enhances the disorder over crystals containing the pure (R,R <u>or</u> S,S) arrangements. The racemic system studied in the present work is τ-(P-(r)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (hereafter τ(r)-AuBr$_2$). The compound τ-(P-(R,R)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ was also investigated yielding very similar results to τ-AuBr$_2$.

In this investigation, single crystals of τ-phase materials (square plates of average size $1 \times 1 \times 0.2 \ mm^3$) were grown by electrochemical methods. Resistance measurements were four-terminal, inter-plane or in-plane measurements with current values between 50 nA and 300 μA. Electrical contact was made to the samples with 25 micron gold wires connected with carbon or silver paint. A tunnel diode arrangement was used for the skin-depth study, and a calorimeter platform in an evacuated capsule was employed for the magnetocaloric study. Experiments were carried out at the National High Magnetic Field Laboratory (NHMFL) DC field facilities in Tallahassee, and at NHMFL-Los Alamos with pulsed magnets.

The high field magnetoresistance of the τ-phase materials has been investigated in a dc hybrid magnet up to 45 T (Fig. 2), and in pulsed fields (6 ms rise-time) up to 60 T (Fig. 3). In all cases where the pyrazino (N-N) materials were investigated, a transition between a metallic state and a highly insulating state is observed at a threshold field B_{th}. In Fig. 2a the inter-plane magnetoresistance for $\tau - AuI_2$, is shown for low temperature ac transport data. For fields above B_{th}, the inter-plane resistance R_{zz} increases by orders of magnitude, and in some cases becomes un-measurable by conventional transport methods. B_{th} is temperature dependent, and moves to higher fields with increasing temperature. The Shubnikov-de Haas (SdH) effect, which has been studied
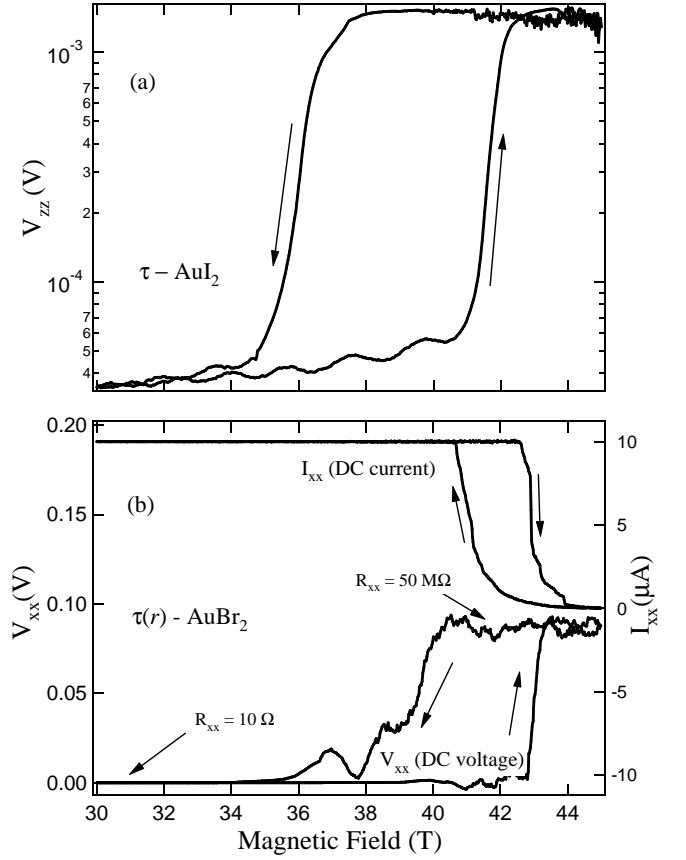

FIG. 2: a) Inter-plane (V_{zz}) ac resistance data in dc magnetic fields on τ-AuI$_2$ at 0.5 K. Shubnikov-de Haas oscillations are observed below the threshold field. b) In-plane (V_{xx}) dc resistance and current measurements for τ(r)-AuBr$_2$ in dc magnetic fields. The current (supplied by a constant current source with a 1 volt compliance) vanishes above 44 T due to the very high resistance of the sample. Estimated resistance values for both the metallic and insulating states are indicated.

previously[11] in $\tau - AuBr_2$, is observed below B_{th} in this case. In Fig. 2b we show an in-plane dc measurement of V_{xx} on $\tau(r) - AuBr_2$ where the current is also monitored. We find that the current vanishes in the high field insulating phase.

Inter-plane measurements of $\tau(r) - AuBr_2$ in pulsed magnetic fields are shown in Fig. 3. In Fig. 3a we show the simultaneous voltage and current signals. The transition, due to the extremely abrupt increase (or decrease) of impedance of the sample upon entering (or leaving) B_{th}, causes the current to vanish (or reappear) on a short time scale comparable to the response time of the coaxial leads. The strange appearance of the voltage signal, which is characteristic of pulsed field measurements for these materials, is primarily the result of the current going to zero on the up-sweep. The resistance, as noted in the figure, is obtained from the ratio V_{zz}/I_{zz}. In Fig. 3b we show a detail of the insulator-to-metal signal for a sys-
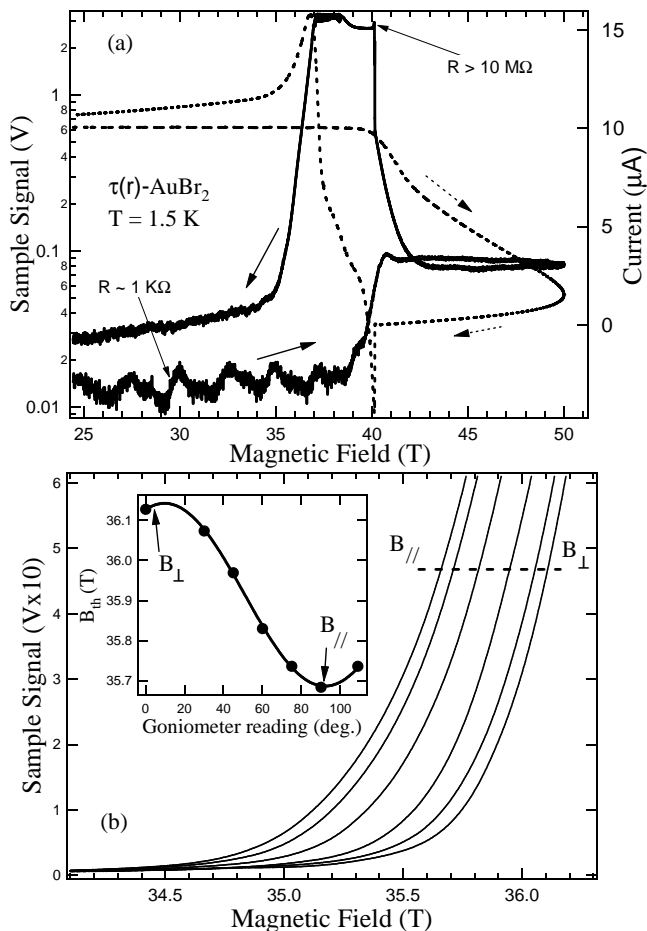
FIG. 3: Inter-plane (R_{zz}) dc magnetoresistance studies of the high field transition in pulsed fields. a) Simultaneous measurement of sample voltage (solid line) and current (dashed line) in $\tau(r) - AuBr_2$ at 1.5 K. Due to the fast time scale of the measurement, the abrupt change in the sample resistance produces dynamic changes in the current, although the current does vanish in the insulating state. Estimated resistance values for both the metallic and insulating states are indicated. b) Field orientation dependence of the threshold field for the insulator-to-metal (down sweep) transition. Inset: values for B_{th} vs. angle determined at a constant signal level (dashed line).

tematic variation of field directions from B//c to B//a-b plane. Both hybrid and pulsed field results indicate that B_{th} decreases only slightly as the field is tilted into the a-b plane. In contrast, for an orbital effect, the threshold field should increase as $1/cos(\theta)$.

To address the bulk-like nature of the transition, a $\tau(r) - AuBr_2$ sample was investigated in a tunnel diode configuration where the axis of the inductor coil and the c axis of the sample were co-linear with the applied field. Hence the ac field of the 43 MHz coil was perpendicular to the conducting layers of the sample. In this configuration, a finite skin depth of the ac field (typically about 1000 μm for in-plane conductivity in an organic

conductor for this frequency range) will reduce the resonant frequency of the TDO oscillator.[12] Measurements were carried out at both high temperatures above the transition (18 K) to obtain a background signal, and at low temperatures where the transition was observed. The results are shown in Fig. 4a for the change in frequency of the TDO vs. magnetic field. The results show that the lower frequency observed in the metallic state increases, essentially to an "empty coil" value, above B_{th}. From this we deduce that the skin depth becomes larger than the coil, i.e., the sample is a bulk insulator.

We have further explored the bulk thermodynamic nature of the transition in terms of the magnetocaloric effect, which has been carried out under quasi-adiabatic conditions both in pulsed fields and in the hybrid magnet. As shown in Fig. 4b for the hybrid magnet, we observe an increase in the sample temperature as B_{th} is crossed for <u>both</u> directions. This result eliminates the possibility that the transition is governed by a Clausius-Clayperon type phase boundary with a latent heat, since for decreasing field through B_{th} the sample temperature should decrease. Rather, the thermodynamics is governed by a hysteresis-loop type of transition where the magnetic field does work on the system, regardless of sweep direction. For quasi-adiabatic conditions, a simple hysteresis model (based on the functional form shown in Fig. 2a) yields a temperature signal very similar to that shown in Fig. 4b, and magnetization measurements are underway to further confirm this picture[18].

Clearly, magnetism is a possible source of the high-field hysteretic behavior. Evidence for weak ferromagnetism has been reported in the EDO class of τ-phase materials[13, 14, 15]. (We note however that concurrent measurements [18] in this investigation have determined that the EDO class of τ-phase materials, where O-O replaces the N-N site in the donor molecule, show only a weak tendency towards an insulating state above 36 T.) In addition, band magnetism has recently been suggested by Arita et al.[16], based on consideration of the very flat, narrow ($E_F \approx 8meV$) bands that appear at the Fermi level from the tight binding calculations. Although magnetization studies have shown a small (0.001 μ_B/formula unit) moment, no hysteresis has been observed in low-field magnetization data[14]. Recent far infrared measurements indicate that the methyl groups show disorder, and it has been suggested that this may lead to electronic localization and magnetism at low temperatures[17].

We conclude that the high field metal-to-insulator transition in the τ-phase materials has the following characteristics. It is most pronounced in the N-N form of the donor molecule. By monitoring the current in dc resistance measurements, we have determined that the current vanishes above B_{th} for both inter-plane and in-plane transport. From skin-depth type investigations, we conclude that above B_{th} the sample is a bulk insulator, and from magnetocaloric measurements, the transition
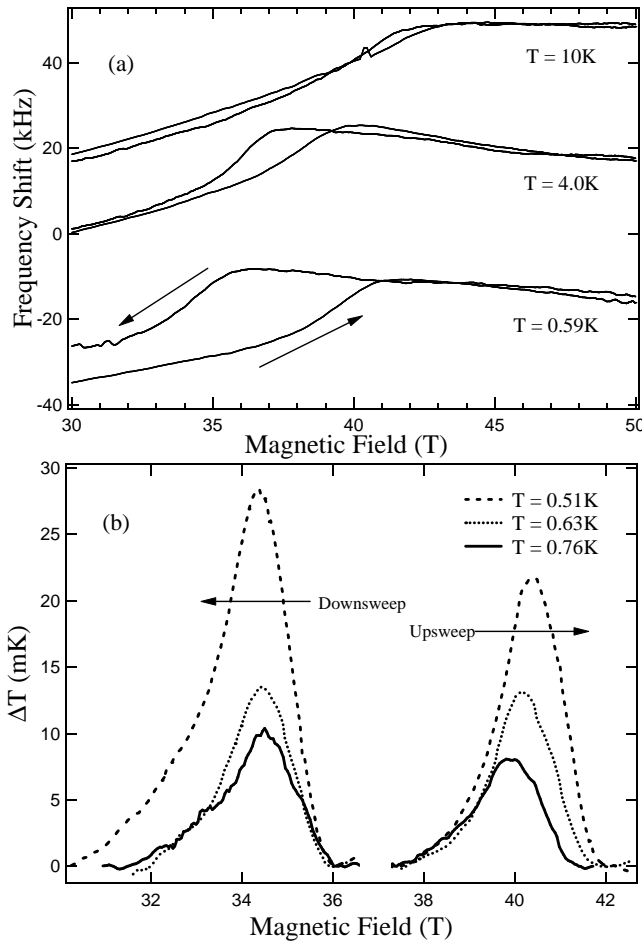
could test for conformational and lattice changes.

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FIG. 4: Bulk properties of the high field transition. (See text for detailed discussion.) a) Response of a tunnel diode oscillator (TDO with background signal removed) at 43 MHz to a $\tau(r)$-AuBr$_2$ sample in the inductor coil in pulsed fields at different temperatures. The sample orientation is $c//H_{dc}//h_{ac}$. b) Magnetocaloric effect (with background signal removed) in dc magnetic fields. A temperature rise is observed for both increasing and decreasing field at the hysteretic metal-insulating transition.

is thermodynamic in nature. Transport measurements in tilted magnetic fields indicate only a weak dependence of B_{th} on orbital effects, which is completely contrary to behavior expected for conventional field induced nesting-type behavior. The origin of the dependent variable (i.e. the analog of χH in the case of ferromagnetism) in the hysteretic loop in the vicinity of B_{th} remains elusive. One possibility would be a metamagnetic-type transition[19] where an anti-ferromagnetic spin system is coupled to the lattice. This would provide the necessary first order nature, required by the magnetocaloric data, for a magnetic transition. The origin may be related to molecular bond and/or conformation effects, given the N-N specificity of the insulating transition. An investigation of the molecular structure above 36 T, for instance by x-ray diffraction,

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